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UTILITY  
PATENT APPLICATION  
TRANSMITTAL

Attorney Docket No.	LAW917
First Inventor or Application Identifier	Harry W. Deckman, et al.
Title	ELECTRIC POWER GENERATION WITH HEAT EXCHANGED MEMBRANE REACTOR
Express Mail Label No.	EJ702278944US

(Only for new nonprovisional applications under 37 C.F.R. § 1.53(b))

## APPLICATION ELEMENTS

See MPEP chapter 600 concerning utility patent application contents.

ADDRESS TO: Assistant Commissioner for Patents  
Box Patent Application  
Washington, DC 20231

1. ☒ \* Fee Transmittal Form (e.g., PTO/SB/17) (Submit an original and a duplicate for fee processing)
2. ☒ Specification (preferred arrangement set forth below) Total Pages   
 - Descriptive title of the Invention  
 - Cross References to Related Applications  
 - Statement Regarding Fed sponsored R & D  
 - Reference to Microfiche Appendix  
 - Background of the Invention  
 - Brief Summary of the Invention  
 - Brief Description of the Drawings (if filed)  
 - Detailed Description  
 - Claim(s)  
 - Abstract of the Disclosure
3. ☒ Drawing(s) (35 U.S.C. 113) Total Sheets
4. ☐ Oath or Declaration Total Pages   
 a. ☐ Newly executed (original or copy)  
 b. ☐ Copy from a prior application (37 C.F.R. § 1.53(b)) (for continuation/divisional with Box 16 completed)  
     i. ☐ DELETION OF INVENTOR(S)  
        Signed statement attached deleting inventor(s) named in the prior application, see 37 C.F.R. §§ 1.63(d)(2) and 1.33(b).
5. ☐ Microfiche Computer Program (Appendix)
6. ☐ Nucleotide and/or Amino Acid Sequence Submission (if applicable, all necessary)  
 a. ☐ Computer Readable Copy  
 b. ☐ Paper Copy (identical to computer copy)  
 c. ☐ Statement verifying identity of above copies

## ACCOMPANYING APPLICATION PARTS

7. ☐ Assignment Papers (cover sheet & document(s))
8. ☐ 37 C.F.R. § 3.73(b) Statement (when there is an assignee) ☐ Power of Attorney
9. ☐ English Translation Document (if applicable)
10. ☐ Information Disclosure Statement (IDS)/PTO-1449 ☐ Copies of IDS Citations
11. ☐ Preliminary Amendment
12. ☒ Return Receipt Postcard (MPEP 503) (Should be specifically itemized)
13. ☐ \* Small Entity Statement(s) (PTO/SB/09-12) ☐ Statement filed in prior application, Status still proper and desired
14. ☐ Certified Copy of Priority Document(s) (if foreign priority is claimed)
15. ☐ Priority of application Serial No. \_\_\_\_\_ Filed on \_\_\_\_\_ in \_\_\_\_\_  
 \_\_\_\_\_ (Country) is claimed under 35 U.S.C. 119
16. ☐ Other: \_\_\_\_\_

\* NOTE FOR ITEMS 1 & 13: IN ORDER TO BE ENTITLED TO PAY SMALL ENTITY FEES, A SMALL ENTITY STATEMENT IS REQUIRED  
 (37 C.F.R. § 1.27), EXCEPT IF ONE FILED IN A PRIOR APPLICATION IS RELIED UPON (37 C.F.R. § 1.28).

# 16. FEE CALCULATION

CLAIMS AS FILED				
(1) For	(2) Number Filed	(3) Number Extra	(4) Rate	(5) Basic Fee \$690.00
Total Claims	32 - 20	12	x 18.00	216.00
Independent Claims	2 - 3	0	x 78.00	0
Multiple Dependent Claim Fee			+ 260.00	0
TOTAL FILING FEE				\$906.00

- ☐ Fee for recording Assignment (\$40.00).
- ☒ Please charge Deposit Account No. 05-1330 in the amount of \$ 906.00 .
- ☒ The Commissioner is hereby authorized to charge any additional fees under 37 CFR 1.16 and 1.17 which may be required during the entire pendency of the application, or credit any overpayment, to Deposit Account No. 05-1330. A duplicate copy of this Form is enclosed.

# 17. If a CONTINUING APPLICATION, check appropriate box, and supply the requisite information below and in a preliminary amendment:

☐ Continuation ☐ Divisional ☐ Continuation-in-part (CIP) of prior application No.: \_\_\_\_\_ / \_\_\_\_\_

Prior application information: Examiner: \_\_\_\_\_ Group / Art Unit: \_\_\_\_\_

**For CONTINUATION or DIVISIONAL APPS only:** The entire disclosure of the prior application, from which an oath or declaration is supplied under Box 4b, is considered a part of the disclosure of the accompanying continuation or divisional application and is hereby incorporated by reference. The incorporation can only be relied upon when a portion has been inadvertently omitted from the submitted application parts.

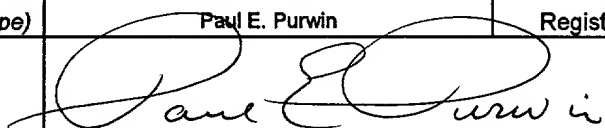
# 18. CORRESPONDENCE ADDRESS

☐ Customer Number or Bar Code Label

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or ☒ Correspondence address below

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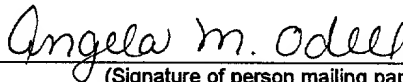
Name (Print / Type)	Paul E. Purwin	Registration No. (Attorney / Agent)	29,203
Signature			Date
			June 29, 2000

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APPLICATION FOR UNITED STATES PATENT

ELECTRIC POWER GENERATION WITH HEAT EXCHANGED  
MEMBRANE REACTOR (LAW917)

Applicants: Harry W. Deckman  
John Fulton  
Jeff Grenda  
Frank Hershkowitz

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## ELECTRIC POWER GENERATION WITH HEAT EXCHANGED MEMBRANE REACTOR (LAW 917)

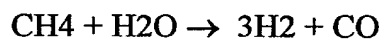
### FIELD OF THE INVENTION

### BACKGROUND OF THE INVENTION

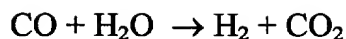
I. This invention relates to heat exchanged hydrogen membrane reactors. More particularly, the invention relates to a hydrogen membrane reactor that employs catalytic or steam reforming and a water gas shift reaction on one side of the membrane, and hydrogen combustion on the other side of the membrane. A portion of the heat of the highly exothermic hydrogen combustion is exchanged through the membrane to supply heat to the reforming reaction. The hydrogen combustion product is used to power a turbine for producing electricity.

#### II. Description of the Related Art

Steam reforming to produce elemental hydrogen is generally known in the art. An idealized steam reforming reaction for a methane feed is represented by the equation:



The above-described reforming reaction is highly endothermic, having a heat of reaction of approximately 88,630 BTU/Mole. Reforming reactions of other hydrocarbon feeds are similarly endothermic. Water Gas Shift reactions to produce hydrogen from carbon are also generally known in the art. An idealized water gas shift reaction for a CO feed is represented by the equation:



This is a mildly exothermic reaction, having a heat of reaction of approximately -17,698 BTU/Mole.

Hydrogen permeable membranes are also generally known in the art, and have been utilized in hydrogen separation in varied applications. The present invention however, utilizes a hydrogen membrane in a novel reactor configuration that is particularly adapted to combust the hydrogen and use its heat of combustion in the hydrogen producing reaction while using the energy of combustion to power or turbine.

#### SUMMARY OF THE INVENTION

The present invention is directed to a heat exchanged membrane reactor that (A) separates hydrogen from a hydrocarbon source using a membrane, (B) combusts the hydrogen, (C) transmits a portion of the heat of the combusted hydrogen to an endothermic reformer process, (D) uses the product of the hydrogen combustion to power a turbine for power generation. The heat exchanged membrane reactor employs thermal or catalytic steam reforming of a hydrocarbon feed to produce hydrogen, which permeates the reactor membrane to the opposite side, where it is combusted. A portion of the heat of combustion is transmitted through the membrane to supply heat to the reforming reaction, a highly endothermic reaction. The combustion product is used to power a turbine for generating electricity. In a further embodiment, a water gas shift reaction is employed on the reformer side of the membrane reactor to convert CO to CO<sub>2</sub> that may be conveniently sequestered. The heat-exchanged membrane need withstand elevated temperatures, ranging from about 400°C to about 1400°C,

and have hydrogen permeance of at least a portion of the membrane ranging from about 1 Mole/(Meter<sup>2</sup>-Day-Atmosphere of H<sub>2</sub>) to about 10<sup>6</sup> Moles/(Meter<sup>2</sup>-day-atmosphere of H<sub>2</sub>). In a preferred embodiment, the reforming reaction and at least a portion of the hydrogen combustion occurs proximate to the membrane to facilitate the heat transfer.

## BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is across sectional view of an embodiment of the heat exchange membrane reactor.

Figure 2 is a diagram that illustrates the use of the heat exchange membrane reactor powering a gas turbine generator.

Figure 3 is a diagram that illustrates the use of the heat exchange membrane reactor powering a gas turbine generation and sequestering CO<sub>2</sub>.

Figure 4 is a cross sectional view of a modular embodiment of the heat exchange membrane reactor.

## DETAILED DESCRIPTION OF THE INVENTION

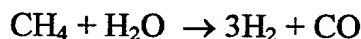
The operation of the heat exchange membrane reactor of the invention may be better understood by reference to the diagram of Figure 1. In figure 1, a reforming feed 1 containing hydrocarbon and water and/or steam is supplied to a "reformer side" 3 of the membrane reactor. A reformer effluent 6 is withdrawn or exits from that side. Compressed air 8 is fed to the combustion side 5 of the membrane, and combustion effluent 9 is withdrawn or exits from that side. In figure 1, the membrane 4 is in the form of a tube and the reforming

side 3 is on the outside of the tube, while the combustion side 5 is on the inside of the tube.

Conventional steam reforming reactions are utilized on the reforming side 3 to react the hydrocarbon with H<sub>2</sub>O to form elemental hydrogen and at least CO. The water and/or steam and hydrocarbon fuel are supplied at pressures ranging from about 1 bar to about 300 bars, and preferably from about 5 bars to about 40 bars to both facilitate hydrogen permeance through the membrane and help maintain structural integrity of the membrane 4. The hydrocarbon feed may comprise any carbon-containing fuel susceptible to thermal or catalytic reforming and/or shift reaction known in the art to produce hydrogen such as carbon monoxide, methane and propane.

For hydrocarbon feeds (i.e., those molecules containing only C and H) there need be at least two moles of water in the feed per moles of carbon feed. Less water causes incomplete conversion and carbon deposition, therefore, it may be desirable to use water feed content ranging from about 1.7 to about 6.0 moles of water per mole of hydrocarbon feed. More preferably, water feed content ranges from about 2 to about 4 moles of water per mole of hydrocarbon feed. For general carbon containing feeds, the steam amount is expressed as a steam to carbon ratio (S/C), which is preferred to be in the range of 1 to 6. More preferably, for carbon containing feeds with overall molar composition expressed as C<sub>x</sub>H<sub>y</sub>O<sub>z</sub>, the steam to carbon ratio is between (2-z/x) and (3-z/x).

Steam reforming is a highly endothermic reaction. For example, reforming a simple methane hydrocarbon feed



has a heat of reaction of about 88,630 BTU/mole. One aspect of the present invention is the utilization of at least a portion of the heat of hydrogen combustion to supply at least a portion of the heat requirements of the reformer's endothermic reaction. To facilitate this, the reforming reaction preferably occurs proximate to or most preferably, at the reformer side surface of the membrane. A means to accomplish this is to promote the reforming reaction using a catalyst that is contiguous with, or deposited on at least a portion of the membrane 4. In one embodiment, a reforming catalyst is deposited onto or into a portion of the surface of the membrane. Figure 1 shows a catalyst (41, 48) deposited onto the surface of the membrane. Examples of materials that are suitable as reforming catalysts include nobel metals and nobel metal oxides such as Platinum, Ruthenium, and oxides thereof, transition metals and transition metal oxides and generally elements or oxides of group VIII metals as well as Ag, Ce, Cu, La, Mo, Mg, Sn, Ti, Y and Zn, or combinations thereof. Preferred catalyst systems include Ni, NiO, Rh, Pt and combinations thereof. These materials may be deposited or coated on the membrane surface or incorporated into the catalyst surface by means known in the art.

As stated above, the feed fuel and water and/or steam feed are at pressures ranging from about one (1) to about three hundred (300) bars, and preferably between about five (5) and forty (40) bars. The operating temperature of the membrane will range from about 400°C to about 1400°C with a preferred operating temperature range of about 700°C to about 1300°C. While the adiabatic upper temperature limit is about 2000°C, present membrane and gas turbine technology have an operating limit of about 1400°C. The operating temperature on the reforming side of the membrane may be up to about 200°C cooler than the temperature on the combusting side. A sufficient level of hydrogen permeance through the membrane is required in the practice of the invention. Hydrogen permeance under operating conditions will range from



about one (1) to about one million ( $10^6$ ) moles ( $\text{m}^2\text{-day-atm H}_2$ ). The permeance referred to is a point permeance that can be defined at each point on the membrane surface and the units atmosphere of  $\text{H}_2$  refer to the difference between the hydrogen partial pressure across the membrane. One skilled in the art will recognize that hydrogen permeance will be influenced by the hydrogen-pressure differential between the reformer side 3 of the membrane and the combustion side 5 of the membrane, the temperature of the membrane 4 and/or hydrogen gas, and strongly influenced by the composition, thickness and configuration or shape of the membrane and membrane surface(s). Because of the wide variation in physical conditions along the length of the membrane, we require that at least one region of or on the membrane has a hydrogen permeance in the range from 1 Mole / {Meter<sup>2</sup>-Day-Atmosphere of  $\text{H}_2$ ) to  $10^6$  Mole / {Meter<sup>2</sup>-Day-Atmosphere of  $\text{H}_2$ ). Suitable membrane materials are ceramics such as alumina and zirconia silicon carbide, silicon nitride, or combinations thereof, including for example,  $\text{Al}_2\text{O}_3$ ,  $\text{ZrO}_2$ ,  $\text{MgO}$ ,  $\text{TiO}_2$ ,  $\text{La}_2\text{O}_3$ ,  $\text{SiO}_2$ , perovskites, hexaaluminates, and metals such as nickel and high nickel content alloys, and cermets.

Membranes may be incorporated into a module. Several technologies exist to form membrane combustor modules. Membrane modules provide means to combine multiple membrane elements with a gas distribution means and with flow passages or channels that bring the gases into close proximity to the membrane. Membrane elements may be fabricated in many ways, including as tubes and flat plates. Module technologies suitable for various membrane elements are known in the art.

Within the module, the membrane may be in the form of a flat sheet, tube, hollow fiber, or may be integrated into a monolithic structure. The membrane is sealed to or into the module so that the feed and permeate are

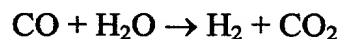
separated from each other by the membrane. In a preferred embodiment the membrane is sealed into the module so that the feed and permeate streams are separated. In this embodiment the module provides a method of distributing and collecting separate feed and permeate streams from individual membrane elements. The membrane elements may be formed as a symmetric or asymmetric structure. The membrane may also have a catalytic functionality incorporated into it. Catalyst functionality may be provided as pelletized or powder catalyst, supported or unsupported, that is loaded into the gas passageways proximate to the membrane, or catalyst, supported or unsupported, may be applied directly to the membrane surfaces, or as a porous layer integral with the membrane. Catalyst functionality may be provided in multiple ways and on either or both sides of the membrane.

In a preferred embodiment, heat exchange membrane 4 comprises an asymmetric membrane having a relatively porous support or substrate and a thin separation layer that selectively diffuses hydrogen. The porous support, illustrated in Figure 1 as 42, provides mechanical strength and structural integrity as well as facile transport of molecules to the separation layer 43. The porous support may be composed of multiple layers of material, each with a differing chemical composition or pore size. In a preferred embodiment, the majority of pores in the support are in the range from .05 to 30  $\mu\text{m}$ . Materials that can be used for supports include alumina, zirconia, silicon carbide, and porous metals such as porous steel, nickel and alloys such as Hasteloy. The support structure is preferably stable under high temperature operating conditions and must not be degraded by molecular species that are utilized or formed in the process (for example steam). The membrane 4 illustrated in Figure 1 is comprised of catalyst (41,48), porous support 42, and permselective layers 43. Catalysts 41 and 48 may comprise two or more catalysts, one serving

to catalyze the steam reforming reaction, the second to catalyze the water gas shift reaction.

A thin selective diffusion layer, illustrated in Figure 1 as **43**, may be positioned on or into the combustion side surface of the membrane. This is most preferable when, for example, hydrocarbon feeds contain materials that would be deleterious to such material. The thin selective diffusion layer may comprise a thin film of metal such as nickel, or ferrous alloys or inorganic materials such as alumina, zirconia, yttrium stabilized zirconia, silicon carbide, silicon nitride, perovskites and hexaaluminates ranging in thickness from about 100 angstroms to 500 microns. The asymmetric configuration facilitates high hydrogen permeance while maintaining hydrogen selectively and structured integrity under the contemplated operating temperatures and pressures.

In a preferred embodiment, the steam reforming reaction is followed by a water shift gas reaction on the reformer side **3** of the membrane reactor. This reaction, generally known to those skilled in the art, converts carbon monoxide into a carbon dioxide. An idealized reaction is represented by the formula:



The reaction is mildly exothermic having a heat of reaction of approximately -17,700 BTU/mole. As practiced in the art, water gas shift is accomplished in two stages, at high and low temperature, respectively. In the first (high temperature) stage, the reaction is conducted with chromium promoted iron catalyst at an inlet temperature of about 370°C. Reaction exothermically raises the temperature to about 430°C at the exit. A second stage

of low temperature shift is then employed because equilibrium toward hydrogen is improved at lower temperature.

In a preferred embodiment of the present invention, permeation of hydrogen through the membrane is used to drive the equilibrium, instead of using lower temperature. This permits deleting the low temperature shift portion, and permits the user to run the high temperature shift at higher temperatures. In one embodiment, the catalyst used for steam reforming is also used to catalyze the shift reaction, and shift and reforming reactions occur in parallel according to their individual rates at locations along the reforming side of the membrane.

In the preferred embodiment, the feed flow of fuel and steam on the reformer side is in a direction opposite to the feed flow of air on the combustor side. (This arrangement is commonly referred to as counterflow.) Counterflow is preferred because it matches the cooling of the carbon dioxide to the pre-heating of the combustion air, and is also preferred because it matches the hottest portion of the combustion side with the reforming reaction, which is endothermic. Other arrangements such as co-flow or crossflow, both generally known in the art, may be used, for example for mechanical or chemical reasons.

In a preferred embodiment, the catalyst for the water gas shift reaction is contiguous with or deposited on at least a portion of the surface of the heat exchange membrane. In this embodiment, steam reforming chemistry occurs first, illustrated as zone 71 in Figure 1, and shift reactions occur second, illustrated as zone 72. In zone 71, steam-reforming reactions occur in the area 31 that is proximate to the membrane, and/or catalyzed by steam reforming catalyst 41. In zone 72, shift reactions occur in the area 32 that is proximate to the membrane, and/or catalyzed by shift catalyst 48. In this arrangement, heat 62

released by the shift reaction may be conducted to the combustion side 52 where it may provide preheat for the incoming air stream 8. Combustion of hydrogen in the region 51 of zone 71 provides heat 61 that is conducted to side 31 to provide the heat of the reforming reaction.

Hydrogen liberated or produced in the reforming reaction and the water gas shift reaction selectively permeates the membrane 4 to the combustion side 5 of the reactor. Selectively permeates, simply stated, means that the membrane porosity permits the diffusion of the relatively small size hydrogen molecules through the membrane, while blocking the flow of the other gases. Flux of hydrogen is from the reforming side 3 to the combustion side 5 and is illustrated in figure 1 with arrows 21 and 22.

It is preferred that, at areas of maximum hydrogen permeance, the hydrogen selectivity be at least 3:1 with respect to other gases such as nitrogen, oxygen, methane, CO, CO<sub>2</sub> and H<sub>2</sub>O. In a preferred embodiment, the foregoing selectivity ratio is at least about 100:1. More preferred is a selectivity ratio of at least about 10000:1.

The remaining process stream 6 will substantially comprise carbon dioxide (CO<sub>2</sub>). Having substantially isolated the CO<sub>2</sub> stream, this gas stream may be sequestered by such means as, adsorption or containment, injection into reservoirs such as deep wells, deep ocean injection, and the like. Therefore, in accordance with one aspect of the present invention, a process stream substantially comprised of CO<sub>2</sub> is isolated and available for sequestration by means known in the art.

As stated above, the hydrogen produced or liberated in the reforming reaction and water gas shift reaction permeates the heat exchange membrane 4 to

the combustion side 5 of the reactor. The hydrogen is then combusted proximate to the heat exchange membrane 4. This is done to facilitate transfer of the heat of combustion of the hydrogen through the heat exchange membrane 4, to supply heat to the reforming reaction. In a preferred embodiment, at least a portion of the surface or surface region of the combustion side surface of the heat exchange membrane contains a catalyst for the combustion of hydrogen. This catalyst is most preferably on a portion of the surface or surface region of the membrane 4 that is juxtaposed the region where the stream reforming reaction occurs.

Catalysts that are suitable for use in the oxidation of hydrogen (i.e., combustion) of the invention include mixtures of metals and/or metal oxides from the transition elements as well as from groups 2a, 3a, and 4a of the periodic table (including Lanthanides and Actinides). Such catalysts may take on the conventional format of catalyst on support, however at the high temperature of operation utilized for the present invention, catalyst may take the form of a single mixed-metal oxide formulation, such as a substituted perovskite or hexaaluminate. Catalyst systems developed for catalytic combustion in gas turbines are particularly useful in the present invention (for example, see Catalysis Today, Volume 47, Nos. 1-2(1999)). Preferred support materials include oxides of elements in groups 2a, 3a 3b (including Lanthanides), 4a, and 4b. More preferred support materials include  $\text{Al}_2\text{O}_3$ ,  $\text{TiO}_2$ , and  $\text{ZrO}_2$ , especially as stabilized, for example with rare-earth oxides. Also more preferred are hexaaluminate supports including  $\text{LaAl}_{11}\text{O}_{18}$ , (more generally  $\text{MAl}_{11}\text{O}_{19-\alpha}$ , where M is an element or mixture of elements, for example including La, Ba, Mn, Al or, Sr). Also more preferred are perovskite supports such as  $\text{LaCrO}_3$  (more generally  $\text{M1M2O}_{3-\alpha}$ , where M1 and M2 are each an element or mixture of elements, for example including Fe, Ni, Co, Cr, Ag, Sr, Ba, Ti, Ce, La, Mn, Zr). Substituted hexaaluminate, perovskite, or mixed metal oxide supports may, in

themselves, provide adequate catalytic activity for high temperature oxidation of hydrogen. Alternatively, a catalytic agent may be dispersed onto the support. Preferred catalyst materials include metals and oxides of elements in groups 6b, 7b, and 8. More preferred catalyst materials include metals and oxides of elements in groups 6b, 7b, and 8. More preferred catalyst materials are the group 8 metals and oxides, in particular metals and oxides of Fe, Rh, Pd, and Pt. Metals and oxides of Fe and Pd are most preferred for reasons of least volatility at high temperatures.

In addition to providing heat to the reforming reaction, the hydrogen combustion reaction produces energy. In one embodiment, this energy is utilized to power a turbine for the production of electricity. As illustrated in Figure 1, compressed air 8 is fed to the combustion side of the reactor. The pressure of the compressed air may range from about three (3) bars to about three hundred (300) bars and preferably between about eight (8) bars and about fifty (50) bars. Because the combusted fuel is hydrogen, the combustion produces substantially no carbon dioxide product to be of concern regarding the greenhouse effect on the environment. Nor does effluent 9 contain substantial amounts of carbon monoxide or unburnt hydrocarbons of concern to the environment. In addition, the use of hydrogen as fuel provides wide process latitude regarding combustion stoichiometry and temperature. Combustion at relatively lean, cool (compared to stoichiometric combustion) conditions in proximity to the membrane will produce substantially no nitrogen oxide products. In this embodiment, the combustion energy powers a turbine for the production of electricity.

Referring now to Figure 2, there is illustrated a heat exchange membrane reactor powered turbine for the production of electricity. The membrane reactor has a reformer side 3 and combustion side 5 separated by a

heat exchange membrane 4. A hydrocarbon plus water (steam) feed 1 is supplied to the reformer side of the reactor. Hydrogen produced in the reforming reaction and the water gas shift reaction permeates membrane 4 to the combustion side 3 of the reactor. Compressed air 8 is fed to the combustion side 3 of the reactor where hydrogen from the reformer reaction and water gas shift reaction has permeated to. The hydrogen is combusted; its combustion energy released into combustion product 9, which is directed to turbine expander 204. In some embodiments of the present invention, all or a fraction (215) of the reforming-side reaction product 6 is combined with combustion effluent 9 as a combined stream 203 that is directed to the turbine expander 204. Turbine expander 204 produces power on shaft 206, which power provides the compressive energy to compress air stream 201 via compressor 202, and which power is used to produce electricity in generator 207. The expanded combustor effluent 205 contains waste heat that can be recovered by raising steam and preheating feeds. In this embodiment, waste heat boiler 212 removes heat from the combustor effluent 205, and provides that heat to boiler feed water 211 to raise steam 213 that is fed to the reforming side of the reactor. Cooled combustor effluent 208 may be discharged to the atmosphere. .

The reforming effluent 6 may be used in several ways. In a preferred embodiment, it is cooled in heat exchanger 216, increased in pressure via compressor 220, and finally sequestered as stream 221. Depending on steam/carbon ratios and other operating parameters, liquid water may need to be removed at some point in the cooling, compressing and sequestering of the reforming effluent. Such removal is well known in the art. In some embodiments, a portion 217 of the cooled reforming effluent is made into a higher-pressure stream 219 via compressor 218 and is recycled to the reformer feed. The combined reformer feed 1 consists of hydrocarbon feed 214, steam 213, and optionally recycled reformer effluent 219. The combined stream is



preferably heated prior to introduction into the reactor, for example using heat exchanger 232. Heat exchanger 232 could be a furnace or could be heat recovery from effluent streams such as 6 or 205, some combination of furnace and heat recovery. Arranging such heat recovery is well known in the art.

A differential pressure ( $\Delta P$ ) may exist between reforming side and the combustion side of the membrane. Differential pressure is characterized in two ways; the magnitude of the pressure difference and the sign of the pressure difference (which stream is higher pressure). Both of these characteristics may vary with application.

In some embodiments of the present invention, it will be preferred for the reformer to be at higher pressure than the combustor. For example, when the objective is to combust methane and leave a sequesterable  $\text{CO}_2$  stream, it may be preferred to have the reforming side at substantially higher pressure than the combustion side. When the pressure of the reformer is higher than the combustor, the magnitude of that pressure difference is preferred to be less than about 100 bar.

In some embodiments of the present invention, it will be preferred for the combustor to be at higher pressure than the reformer. For example, when the objective is to use a low pressure fuel gas as turbine fuel without expending the cost of compressing that fuel gas, it may be preferred to have the reforming side at substantially lower pressure than the combustion side. In such an embodiment, a near-surface combustion of hydrogen on the combustor side creates a local low  $\text{H}_2$  partial pressure, which enables transfer of the  $\text{H}_2$  from the low-pressure reformer side to the high-pressure combustor side. When the pressure of the combustor is higher than the reformer, the magnitude of that pressure difference is preferred to be less than about 50 bar.

When the magnitude of the pressure difference is large (for either sign), then there may be debits associated with the required mechanical strength and the differences between volumetric flow rates between the two sides. For example, large pressure differences call for devices physically capable of supporting the forces associated with the high differential pressure. In some embodiments, the incentive of large differential pressure will justify the added complexity and cost of the configuration, in other applications it may not. Thus, for some embodiments, it is preferred that the differential pressure ( $\Delta P$ ) between reforming side and the combustion side of the membrane be less than about 5 bars. For some embodiments it is preferred that the differential pressure ( $\Delta P$ ) between reforming side and the combustion side of the membrane be less than about 20% of the higher of the two pressures.

The present invention may operate with feeds that may contain hydrocarbons, oxygenates, CO, CO<sub>2</sub>, nitrogen, hydrogen, H<sub>2</sub>S, sulfides, mercaptans, and thiophenes. Other trace components may also be present in the feed. The product from the reformer side will contain CO<sub>2</sub> and H<sub>2</sub>O. A substantial portion of the H<sub>2</sub>O exiting the reformer originates as feed. The CO<sub>2</sub> in the gas exiting the reformer is the sum of the net amount produced in the reforming reaction and the amount originating with the feed. Other components that can be present are products that can be produced in the reforming reaction such as CO and hydrogen. The nitrogen level in the reformer product will be determined by the nitrogen level in the feed. The level of H<sub>2</sub>S in the product gas from the reformer will be determined by the amount of sulfur in the feed.

The ability to produce a stream that has a significant CO<sub>2</sub> concentration is one aspect of the invention. A significant CO<sub>2</sub> concentration

can be produced when the feed contains less than about 35 mole % nitrogen and, in a preferred embodiment, less than 5 mole % nitrogen. When there is a substantial amount of CO<sub>2</sub> in the product gas, it may be economically disposed, stored, or utilized in underground formations. For example, product CO<sub>2</sub> may be utilized as an enhanced recovery fluid in oil reservoirs or may be sequestered in depleted oil or gas reservoirs. Certain aquifer formations are suitable for storing or sequestering CO<sub>2</sub>. Because of the pressures in underground formations, in most cases the CO<sub>2</sub> has to be injected at high pressures. The cost of compression is substantially reduced when the stream exiting the reformer is substantially composed of CO<sub>2</sub>. To minimize the cost of compression, it is advantageous to have the CO<sub>2</sub> rich stream exit the reformer at pressures above 100psi and more preferable at pressures above 250 psi.

Another aspect of the invention is the potential to operate the membrane combustor in a mode that produces less NO<sub>x</sub>. NO<sub>x</sub> production in combustion is generally associated with high temperatures. It is possible to operate the membrane combustor at temperatures lower than those normally required to sustain a flame. Lower temperature operation is possible because hydrogen is burned in the membrane combustor rather than a hydrocarbon. Hydrogen can be combusted under conditions where hydrocarbons will not normally react. The combustion of hydrogen may also be facilitated by a catalyst, allowing reaction at highly rich or lean conditions. When the membrane combustor is operated in a mode designed primarily for NO<sub>x</sub> reduction, it may be possible to combine the product streams exiting the reformer and combustion sides. Recombination of these streams may occur within the membrane module or after the streams exit the membrane module and before they are fed into a gas turbine.

By way of illustration, the following exemplify embodiments of the present invention.

**Example 1:**

In the present example, diagrammatically illustrated in Figure 3, methane is combusted in heat exchanged membrane reactor, the reactor feeds and effluents being integrated with a gas turbine for power generation. The gas turbine is comprised of an air compressor 302, a power turbine 304, a shaft 306 and a generator set 307. Air 301 enters the compressor 302 and leaves as a pressurized stream 358 at a pressure of about 35 atmospheres absolute and a temperature of about 600°C. The air travels through the heat exchanged membrane reactor on the combustion side 355 where some of the oxygen reacts with hydrogen that has permeated the membrane 354. The combustion effluent 359 goes to the power turbine 304 where it is expanded to an atmospheric pressure stream 305 at a temperature of about 417°C. Component flow rates for streams 358 and 359 are shown in Table 1. Under these conditions the compressor 302 uses 100 MW of power and the turbine 304 yields 157 MW for a net gas turbine power yield 307 of 57 Megawatts.

The reforming side 353 of the heat exchanged membrane reactor is fed by a methane/steam stream 351 at a steam/methane mole ratio of 2.5 and preheated to 490°C. Within the reactor, the methane is completely converted to hydrogen and CO<sub>2</sub>, the hydrogen permeating to the combustion side 355. The CO<sub>2</sub> and a residual amount of steam comprise the product stream 356 of the reforming side 353. Component flow rates for streams 351 and 356 are shown in Table 1. In the present example, 1.326 kg/sec of H<sub>2</sub> is created and permeated through the membrane 354.

Table 1

**Stream Flows, kg/sec**

Figure 3 Identifier	Reformer Feed 351	Reformer Product 356	Combustor Feed 358	Combustor Product 359
O <sub>2</sub>	0.000	0.000	37.025	26.420
N <sub>2</sub>	0.000	0.000	121.875	121.875
CH <sub>4</sub>	2.651	0.000	0.000	0.000
H <sub>2</sub> O	7.457	1.491	0.000	11.931
CO <sub>2</sub>	0.000	7.291	0.000	0.000
Total	10.108	8.783	158.900	160.226
Temperature, °C	490	800	600	1224

The reformer feed 351 is preheated by recovering heat from several sources. The power turbine exhaust 305, at about 417°C is used in a waste heat boiler 312 to make steam 313 from boiler feed water 311. The cooled exhaust 308, now at about 325°C is then used in heat exchanger 336 to heat the methane fuel 314 from pipeline temperatures of about 25°C to about 250°C, leaving the final flue-gas 335 at about 316°C. The heated methane 330 and the steam 313, both at about 250°C are combined into a feed stream 331, which is heated in heat exchanger 332 against the reformer effluent stream 356. The resulting preheated reformer feed 351 is at about 490°C, while the cooled reformer effluent stream 333 is at about 300°C. This reformer effluent stream 333 is further cooled in air fin heat exchanger 316 to condense water and cool to about 50°C. Compressor 320 is used to raise this CO<sub>2</sub> stream to a high-pressure stream 321 suitable for sequestration.

In this example, the gas turbine net power 307 of 57 MW represents about 43% of the lower heating value of the methane feed 314. This compares favorably with the cycle efficiency of the gas turbine as used with a normal combustor. Because the cooled CO<sub>2</sub> effluent 334 is highly concentrated and at

high pressure, the additional work required to compress to sequestration pressures is minimal. For example, compression to 160 bar would require less than a megawatt of power. Also, the flue gas 335 at about 317°C would be suitable for generation of additional power via combined cycle operation.

## Example 2

The membrane combustor module shown in Figure 4 is formed from asymmetric tubular membranes 401. The tubular membranes are sealed into the module in a geometry similar to a tube in shell heat exchanger. Each tubular membrane is sealed at each end into a plate (403 and 405) in a manner such that gas can pass directly through the plate into the interior 407 of each tube. The plates (403 and 405) are in turn sealed into a ceramic tube 409 that forms the shell of the module. The ceramic tube 409 has fittings (411 and 413) that allow gas to be flowed inside the shell. At the ends of the module there are flanges (417 and 419) that allow the module to be sealed to inlet and exit pipes.

Compressed air 415 in the pressure range of 5 to 40 atmospheres is fed into the shell through fitting 411. The compressed air 415 entering the shell is in the temperature range from 25° to 1000° Centigrade. It is preferred that the compressed air be in the temperature range from 200 to 600 °C. In general air will heat to these temperature ranges when it is compressed.

Within the shell space of the module 421, the oxygen in the compressed air reacts with hydrogen permeating the asymmetric tubular membranes 401, releasing heat and forming water vapor. It may be desirable to catalytically assist the reaction of oxygen and hydrogen. In this example the reaction is catalyzed with a platinum catalyst that is dispersed on the exterior surface 423 of the asymmetric membranes 401. The catalyst can be deposited from solution

Whether a catalyst is used or not, it is preferable to have a substantial portion of the hydrogen permeating the membrane react with oxygen in the compressed air. As the compressed air travels down the length of the module from the inlet port 411 to the exit port 413, it heats up. The air and water vapor exiting the module 425 are preferably at a temperature in the range from 700 to 1400 °C. This hot high-pressure air and water vapor stream 425 is fed to a gas turbine where electric power is produced.

In the interior of the tubular asymmetric membranes, a feed 427 containing H<sub>2</sub>O and methane is flowed in a direction that is countercurrent to the hot high pressure air and water vapor stream 425. The hydrocarbons and sulfur species in the feed 427 come from natural gas. The feed 427 also contains a portion of the reformed gas exiting 429 the tubular membranes. The reformed gas 429 is primarily composed of CO<sub>2</sub> and H<sub>2</sub>O. A portion of this gas is recycled back to the input 427 to add CO<sub>2</sub> to the feed. The addition of CO<sub>2</sub> helps suppress carbon deposition within the tubular membrane. In particular, it helps control carbon deposition caused by the Boudart reaction. It is preferred that the amount of gas recycled back to the feed 427 be .1- 50 volume % of the amount of natural gas fed. It is more preferred that the amount of gas recycled back to the feed be in the range of 2-20 volume %. The molar ratio of H<sub>2</sub>O to

CH<sub>4</sub> in the feed, also known as the steam/methane ratio can range from 1 to 6. The steam/methane ratio is preferred to be greater than 2. When the steam/methane ratio is between 1 and 2, all of the carbon cannot be converted to CO<sub>2</sub> and a syngas product can be produced.

The feed 427 pressure of the gas mixture used to fuel the membrane combustor can be in the range from 1-200 atmospheres. It is preferred that the gas mixture be in the range from 2-50 atmospheres. The inlet temperature of the feed 427 can be in the range from 20-700 °C. It is more preferred that the feed is a single-phase, gaseous stream at temperature above 250°C.

As the feed gas 427 travels countercurrently to the compressed air stream (415 and 425), it heats up. As the feed gas heats up it begins to react to form hydrogen. The initial reaction will be predominantly a steam reforming reaction that can be promoted by a catalyst. Further down the module, CO formed by the initial steam reforming reaction is converted to hydrogen and CO<sub>2</sub> with a water gas shift reaction. This reaction can be catalyzed with a catalyst that is different from the catalyst use to promote the reforming reaction. The catalyst for these reactions can be on the inner surface of the tubular membrane, within the wall of the tubular membrane or introduced as catalyst pellets within the interior 407 of the tubular membrane.

In this example, the membrane combustor module is formed from tubular membrane elements 401. The tubular membranes can have an inner diameter in the range from .1 to 25 millimeters and a wall thickness of .1-10 millimeters. It is preferred that the tube wall 431 be porous. The porous wall improves transport of hydrogen across the membrane and also provides structural strength. The most prevalent pore size is in the range from .01 to 100 μm. In this example the porous tube is made by sintering alpha alumina powder. A thin



membrane that is permselective for hydrogen is formed near or on the inner or outer surface of the tube. In this example, the permselective hydrogen membrane is formed on the outer surface of the tube. The hydrogen selective membrane in this example is a 1  $\mu\text{m}$  thick layer of dense alpha alumina. At the operating temperature of the membrane combustor module, the alpha alumina readily transports hydrogen.

### Example 3

This example follows the same flow diagram and conditions as Example 1, except that it has been adjusted for a feed that has a high level of  $\text{CO}_2$ . The feed in this case has a molar  $\text{CO}_2/\text{CH}_4$  ratio of 2.65. The high level of  $\text{CO}_2$  in the feed results in a higher heat capacity for the reformer effluent 356, which, in turn, means that the reformer feed 351 may be heated to a higher temperature. In this case, a reformer feed temperature of  $610^\circ\text{C}$  is achieved, as shown in Table 2 below. The added  $\text{CO}_2$  diluent results in additional small changes in the heat balance that result in a the need for slightly higher methane feed rate, but also provide a slightly higher flow rate to the power turbine. The combination of these changes results in an efficiency decrease of about 0.4% relative to Example 1. Thus, power is extracted from a highly  $\text{CO}_2$ -diluted stream while maintaining the  $\text{CO}_2$  at high concentration and pressure suitable for subsequent sequestration, and without substantial loss in efficiency.

Table 2

	Stream Flows, kg/sec			
	Reformer	Reformer	Combustor	Combustor
	Feed	Product	Feed	Product
Component				
O <sub>2</sub>	0.000	0.000	37.025	26.304
N <sub>2</sub>	0.000	0.000	121.875	121.875
CH <sub>4</sub>	2.680	0.000	0.000	0.000
H <sub>2</sub> O	7.539	1.508	0.000	12.062
H <sub>2</sub>	0.000	0.000	0.000	0.000
CO <sub>2</sub>	19.562	26.933	0.000	0.000
Total Stream	29.781	28.441	158.900	160.240
Temperature, °C	610	800	600	1224

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**WHAT IS CLAIMED IS:****1. A hydrogen membrane reactor comprising:**

a reaction zone wherein a feed containing at least water and carbon-containing species undergoes a reforming reaction to produce hydrogen,

a combustion zone wherein hydrogen produced in the reaction zone is combusted to produce heat and energy,

a membrane separating said reaction zone and said combustion zone, said membrane functions to permit permeance of hydrogen and transmissions of heat through the membrane,

where said reactor is configured to utilize at least a portion of the heat of the hydrogen combustion in the reforming reaction and at least a portion of the energy to produce electricity.

2. The reactor of claim 1 where the reforming reaction is a steam reforming reaction and said feed is steam and hydrocarbons.

3. The reactor of claim 2 where the reaction occurs proximate to the membrane.

4. The reactor of claim 3 where a catalyst is used to catalyze the steam reforming reaction, said catalyst being selected from the group comprising:

- a. Noble metals and noble metal oxides
- b. Transition metals and transition metal oxides
- c. Group VIII metals
- d. Ag, Ce, Cu, La, Mo, Sn, Ti, Y, Zn, and combinations thereof.

5. The reactor of claim 4 wherein said catalyst is select from the group comprising Ni, NiO, Rh, Pt, and combinations thereof.

e. thereof

6. The reactor of claim 1 wherein said reforming reaction is conducted at a temperature ranging from about 400° to about 1400°C.

7. The reactor of claim 6 wherein said reforming reaction is conducted at a temperature ranging from about 700°C to about 1300°C.

8. The reactor of claim 1 wherein said feed is provided at a pressure ranging from about one (1) bar to about three hundred (300) bars.

9. The reactor of claim 7 wherein said pressure ranges from about five (5) bars to about fifty (50) bars.

10. The reactor of claim 1 wherein said membrane has a hydrogen permeance ranging from about one (1) to about one million ( $10^6$ ) moles/(m<sup>2</sup>-day-atm H<sub>2</sub>).

11.. The reactor of claim 1 wherein the pressure of the reaction zone is from about 0 to 100 bar higher than the pressure of the combustion zone.

12.. The reactor of claim 11 wherein the pressure of the combustion zone is from about 0 to 50 bar higher than the pressure of the reaction zone.

13. The reactor of claim 1 wherein said membrane is fabricated from materials selected from the group comprising alumina, zirconia, silicon carbide, silicon nitride, MgO, TiO<sub>2</sub>, La<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, perovskite, hexaaluminate, high nickel content alloys, Hastelloys, cermets, and combinations thereof.

14.. The reactor of claim 1 wherein said membrane reactor is comprised of one or more modules, each module having: (a) a reaction zone, a combustion zone, and a membrane separating said reaction and combustion zones, (b) a distribution and collection means for said reacting and combustion zones, (c) one or more membranes, (d) flow channels between said membrane elements, and (e) sealing means between combustion and reforming zones .

15. The reactor of claim 1 wherein said membrane is an asymmetric membrane, comprising a porous support having thickness of 0.1 to 10 millimeters and pores of 0.05 to 30 microns, and on one side a selective diffusion layer having thickness of about 100 angstroms to 500 microns.

16. The reactor of claim 15 wherein said asymmetric membrane is a catalytic membrane wherein a catalyst is incorporated on either membrane surface or within or on pore structures of the membrane.

17. The reactor of claim 14 wherein catalyst is incorporated into said channels of the modules.

18. The reactor of claim 1 wherein a catalyst is used to catalyze the combustion of hydrogen,

where said catalyst is selected from the group comprising:

- a. Hexaaluminates, perovskites, and mixed metal oxides,
  - b. Metals and metal oxides of elements in groups 6b, 7b, and 8,
  - c. Metals and oxides of Fe, Rh, Pd, and Pt,
- or combinations thereof

19. The reactor of claim 1 where the effluent of the reaction zone is a concentrated carbon dioxide stream that is cooled, compressed, and injected into a reservoir for sequestration of carbon.

20. The reactor of claim 19 where said concentrated carbon dioxide stream is injected into geological formations to facilitate sequestration of carbon.

21. The reactor of claim 19 where said concentrated carbon dioxide is injected into deep water to facilitate sequestration of carbon.

22. A method for generating power using a heat exchanged hydrogen membrane reactor, comprising the steps of:

- a. supplying a carbon containing feed and water and/or steam to a reformer side of the membrane reactor, said reactor having reactor and combustion zones separated by a membrane;

c. permeating a substantial portion of the hydrogen through the membrane to the combustion zone of the reactor;

23. The method of claim 23 wherein compressed air is supplied to the combustion zone of the reactor whereupon the air is heated by the combustion and the heated air and effluent is used to power a turbine.

24. The method of claim 22 wherein said carbon monoxide is reacted to form carbon dioxide.

25. The method of claim 24 wherein a portion of the carbon dioxide is recycled to the reaction zone to suppress carbon deposition.

26. The method of claim 22 wherein said reacting of the carbon containing feed and water is catalyzed.

27. The method of claim 26 wherein said catalyst comprises:

nobel metals  
nobel metal oxides  
transition metal oxides  
Group VIII metals  
Group VIII metal oxides  
Cz, Ce, Cu, La, Mo, Mg, Sn, Ti, Y, Zr,  
or combination thereof

28. The method of claim 27 wherein said catalyst comprises Ni, NiO, Rh, Pt or combination thereof.

29. The method of claim 27 wherein said catalyst is on or in said membrane.

30. The method of claim 22 wherein said feed and water and/or steam is supplied at a pressure ranging from about one bar to about 300 bars.

31. The method of claim 30 wherein said pressure range from about 5 bars to about 40 bars.

32. The method of claim 23 where said heated air and effluent is at a temperature ranging from about 700 °C to about 1400 °C.



### Abstract of the Disclosure

This invention is directed to a heat exchanged membrane reactor for electric power generation. More specifically, the invention comprises a membrane reactor system that employs catalytic or thermal steam reforming and a water gas shift reaction on one side of the membrane, and hydrogen combustion on the other side of the membrane. Heat of combustion is exchanged through the membrane to heat the hydrocarbon fuel and provide heat for the reforming reaction. In one embodiment, the hydrogen is combusted with compressed air to power a turbine to produce electricity. A carbon dioxide product stream is produced in inherently separated form and at pressure to facilitate injection of the CO<sub>2</sub> into a well for the purpose of sequestering carbon from the earth's atmosphere.

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Figure 1

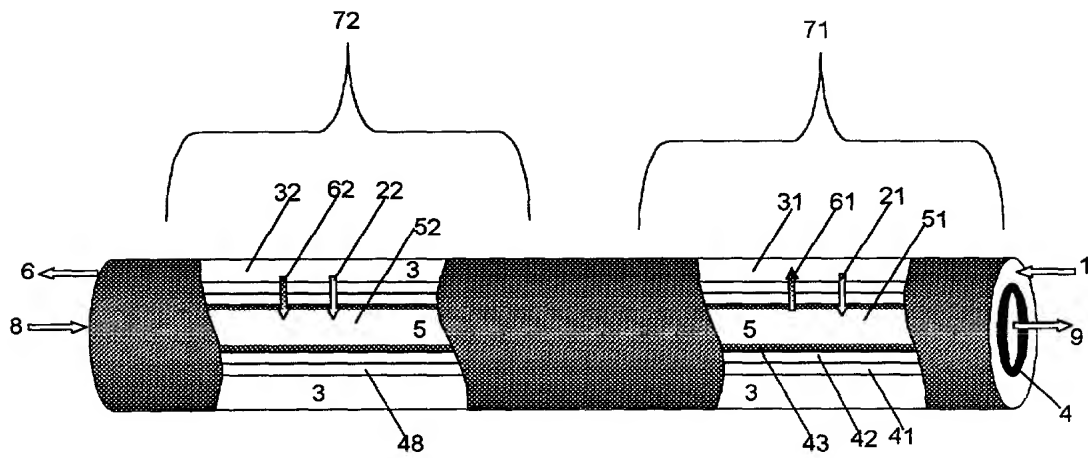
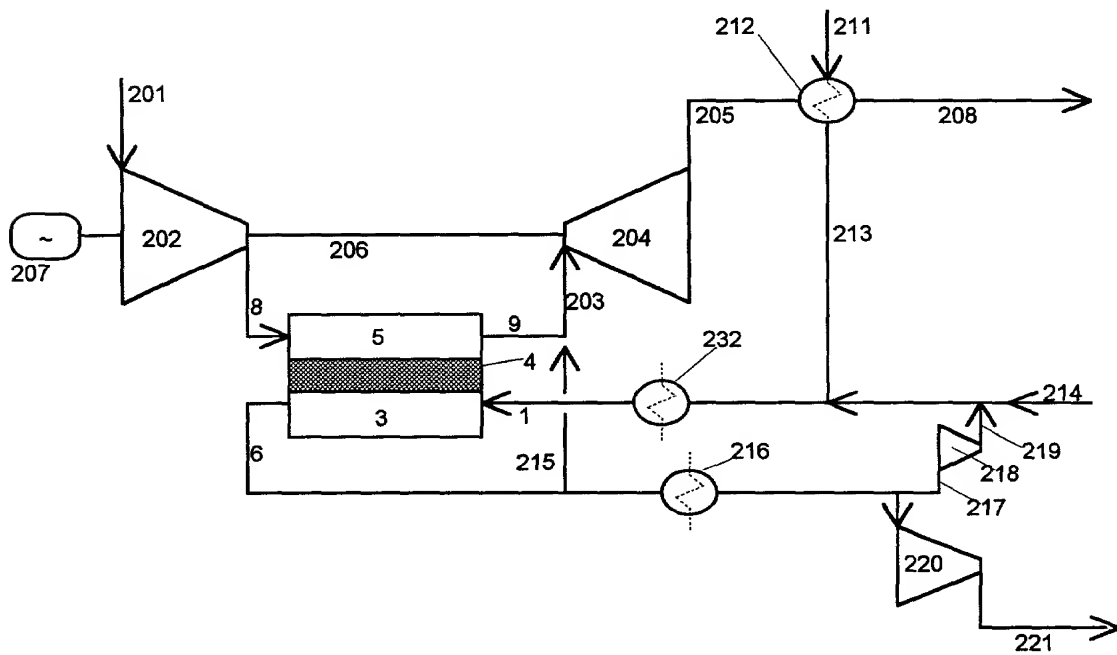
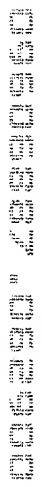


Figure 2:



	1970	1971	1972	1973	1974	1975	1976	1977	1978	1979	1980	1981	1982	1983	1984	1985	1986	1987	1988	1989	1990	1991	1992	1993	1994	1995	1996	1997	1998	1999	2000	2001	2002	2003	2004	2005	2006	2007	2008	2009	2010	2011	2012	2013	2014	2015	2016	2017	2018	2019	2020	2021	2022	2023	2024	2025	2026	2027	2028	2029	2030	2031	2032	2033	2034	2035	2036	2037	2038	2039	2040	2041	2042	2043	2044	2045	2046	2047	2048	2049	2050	2051	2052	2053	2054	2055	2056	2057	2058	2059	2060	2061	2062	2063	2064	2065	2066	2067	2068	2069	2070	2071	2072	2073	2074	2075	2076	2077	2078	2079	2080	2081	2082	2083	2084	2085	2086	2087	2088	2089	2090	2091	2092	2093	2094	2095	2096	2097	2098	2099	2100	2101	2102	2103	2104	2105	2106	2107	2108	2109	2110	2111	2112	2113	2114	2115	2116	2117	2118	2119	2120	2121	2122	2123	2124	2125	2126	2127	2128	2129	2130	2131	2132	2133	2134	2135	2136	2137	2138	2139	2140	2141	2142	2143	2144	2145	2146	2147	2148	2149	2150	2151	2152	2153	2154	2155	2156	2157	2158	2159	2160	2161	2162	2163	2164	2165	2166	2167	2168	2169	2170	2171	2172	2173	2174	2175	2176	2177	2178	2179	2180	2181	2182	2183	2184	2185	2186	2187	2188	2189	2190	2191	2192	2193	2194	2195	2196	2197	2198	2199	2200	2201	2202	2203	2204	2205	2206	2207	2208	2209	2210	2211	2212	2213	2214	2215	2216	2217	2218	2219	2220	2221	2222	2223	2224	2225	2226	2227	2228	2229	2230	2231	2232	2233	2234	2235	2236	2237	2238	2239	2240	2241	2242	2243	2244	2245	2246	2247	2248	2249	2250	2251	2252	2253	2254	2255	2256	2257	2258	2259	2260	2261	2262	2263	2264	2265	2266	2267	2268	2269	2270	2271	2272	2273	2274	2275	2276	2277	2278	2279	2280	2281	2282	2283	2284	2285	2286	2287	2288	2289	2290	2291	2292	2293	2294	2295	2296	2297	2298	2299	2300	2301	2302	2303	2304	2305	2306	2307	2308	2309	2310	2311	2312	2313	2314	2315	2316	2317	2318	2319	2320	2321	2322	2323	2324	2325	2326	2327	2328	2329	2330	2331	2332	2333	2334	2335	2336	2337	2338	2339	2340	2341	2342	2343	2344	2345	2346	2347	2348	2349	2350	2351	2352	2353	2354	2355	2356	2357	2358	2359	2360	2361	2362	2363	2364	2365	2366	2367	2368	2369	2370	2371	2372	2373	2374	2375	2376	2377	2378	2379	2380	2381	2382	2383	2384	2385	2386	2387	2388	2389	2390	2391	2392	2393	2394	2395	2396	2397	2398	2399	2400	2401	2402	2403	2404	2405	2406	2407	2408	2409	2410	2411	2412	2413	2414	2415	2416	2417	2418	2419	2420	2421	2422	2
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